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DEPARTMENT OF MACROMOLECULAR SCIENCE

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Synopsis

Tensile experiments in polystyrene (PS) and poly(methyl methacrylate) (PMMA) conducted at constant strain rate over a wide range of pressure and temperature have shown that a brittle to ductile transition is induced in these amorphous polymers by the superposition of hydrostatic pressure as well as by the raise of the experimental temperature. A detailed stress-strain analysis permits explanation of the mechanism for the brittle to ductile transition in terms of interaction between two competing processes of plastic yielding -- crazing and shear banding phenomena. The crazing and shear banding processes respond quite differently to changes of pressure or temperature, causing shifting of the brittle to ductile transition point to where the craze initiation stress and shear band initiation stress again become equal. The evidence that the brittle to ductile transition pressure becomes lower with increasing temperature refutes a previously suggested concept that the transition relates primarily to mechanical relaxation phenomena.

INTRODUCTION

The mechanical behaviors of polymers as well as other materials are well known to be affected with a great degree by the changes of experimental conditions and sample preparations. An alternation in fracture modes from brittle to ductile with increasing temperature is one of the most significant cases and many aspects on the brittle to ductile transition in polymers have been studied extensively from its practical importance. Vincent[1,2] made considerable efforts to examine the effects of strain-rate and basic material variables such as molecular weight, crystallinity, additives, crosslinking, side-groups, and molecular orientation on the brittle to ductile transition temperature.

In spite of abundant information on factors which influence the brittle to ductile transition, the mechanism of the transition itself has been understood only fragmentarily. In the most cases[1-3], the brittle to ductile transition phenomenon in polymers has been explained phenomenologically on the basis of Ludwick[4] -Davidenkov and Wittman[5] hypothesis, which was originally suggested from the study of the same transition in metals, and which assumes that the brittle fracture and plastic flow are independent processes and the brittle fracture stress and the yield stress become equal at the transition temperature. Therefore, in this concept no microstructural features such as the crazing[6,7] and shear banding phenomena[8], which have been recently recognized to be the most responsible for the fracture process in glassy polymers, have been considered at all. Another disputant point in the polymer transition phenomenon is on the relationship between the brittle to ductile transition and the mechanical relaxation phenomena. Several authors[9-11] have suggested that the brittle to ductile transition always occurs near a glass transition temperature or a lower temperature-relaxation temperature if the polymer exhibits more than one mechanical relaxation. These relationships, however, have been proved not to have a general validity since some polymers are observed to be ductile at the temperature even lower than the lowest temperature-relaxation temperature[1]. In addition to this temperature-induced transition, it has been demonstrated for several polymers that an increased pressure at constant temperature can likewise induce a transition from brittle to ductile[12-16].

In recent publications[17,18], we have reported quantitative studies of the way in which superposition of hydrostatic pressure induces the brittle to ductile transition in amorphous polymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) at room temperature. Based on the detailed stress-strain analysis in this work, it was suggested that the interaction of the plastic deformation processes of crazing and shear bands appears to be the essential mechanism of the brittle to ductile transition phenomenon. Thus, clarification of the pressure dependence of these processes is likely to lead to greater understanding of the transition than is from the mechanistic viewpoint of the Ludwick-Davidenkov and Wittman hypothesis. The main objectives of the present study are to present more extensive data on the effects of experimental pressure and temperature on the brittle to ductile transition point in PS and PMMA and to investigate further the general mechanism and/or factors governing the transition phenomenon. The relationship between the brittle to ductile transition and mechanical relaxation phenomena will also be discussed.

EXPERIMENTAL

As the detailed explanation of the high pressure-tensile apparatus, specimen geometry, and the procedure to obtain true stress-strain curves have already been done in previous publications[17-19], only the essentials and some modifications will be described here.

The materials studied in this study, PS (from the Dow Chemical Co.) and PMMA (from Cadillac Plastic and Chemical Co.), were obtained commercially in the form of extruded rods. All the tensile specimens were machined directly from the as-received rods and the surfaces were carefully polished along the gauge length to minimize possible surface effects in mechanical behaviors. The overall specimen length was 2.40 inch and the reduced gauge section with 1.50 inch R groove was 0.12 inch in diameter. After polishing, the PS specimens were annealed following the method of Bailey[20]. Finally, surface of the gauge section was sealed with Teflon tape and covered with a transparent silicon rubber in order to prevent possible environmental effects due to the surrounding pressure-transmitting fluid or temperature controlling medium.

The apparatus used for the tensile experiments at atmospheric pressure was an Instron machine furnished with a temperature control-chamber which was filled with silicon oil as a medium. To perform the high pressure-measurements at different temperatures, the high pressure-tensile apparatus was equipped with a temperature-control jacket. The test temperature in the both cases was measured with a thermocouple positioned less than 0.3 inch from the tensile specimens, and was controlled within ±1.5°C fluctuation during the experiments. All the tensile tests were conducted at constant strain rate of about 1.30 %/min.

RESULTS AND ANALYSIS

Brittle to Ductile Transition at Atmospheric Pressure

The tensile experiments on PS and PMMA were carried out over the temperature range from -10°C to 105°C at atmospheric pressure. The temperature effects observed on the stress-strain behavior are shown in Fig. 1 for PS and in Fig. 2 for PMMA, respectively. In the case of PS, a drastic change in the stress-strain curve appears about 90°C. The stress-strain curves of the specimens tested below 80°C are characteristic of the development of the process of craze-yielding[21]. In this process an extensive growth of crazes across the gauge length of specimen occurs beyond a critical level of stress (the break in the curve) and the specimens fracture at very low strain and perpendicular to the tensile direction. In PS it is noticeable that the fracture strains and stresses decrease with increasing temperature. In the optical microscope, the well-developed crazes could be observed on the fracture surface and the adjacent side-surfaces. In contrast, the stress-strain curve at 90°C shows a distinct yield point and the specimen exhibits a necking and further cold-drawing. At 97°C, the specimen deforms uniformly without the neck formation similar to rubber-like materials. For all the specimens deformed at or above 90°C, no craze formation could be observed on their side-surfaces.

In the case of PMMA, the change of fracture mode from brittle to ductile occurs much less discontinuously in the vicinity of 50°C, as shown in Fig. 2. Differing from the case of PS, the fracture strain of PMMA in the brittle fracture region increases gradually with temperature. Further, the stress-strain curves do not exhibit craze-yielding, coinciding with the optical observation that only a few and undeveloped crazes could be detected on the side-surface of the fractured specimens.

To elucidate the mechanism of the brittle to ductile transition, the observed stress-strain curves have been further analyzed in the following manner. Figure 3 shows schematically typical stress-strain curves for brittle and ductile fractures. In general, brittle fracture is considered to occur when a specimen fails at its maximum load (at strains less than, say, 20%, in order to exclude rubbers)[1] but we expand this definition so as to include the case of craze-yielding in PS, since there the fracture is caused by the propagation or development of existing crazes, not shear bands, and its fracture strain is less than 3%. For both brittle and ductile fractures, the stress-strain curves show a departure from linearity as indicated by arrows in the figure. From the simultaneous observations of the stress-strain and optical behaviors, we and other research groups have reported that the onset of non-linearity on the stress-strain curve is accompanied by the initiation of crazes in the brittle fracture region[18,21,22] or by the initiation of shear bands in the ductile fracture region[6,18,23]. Therefore, we define the corresponding stresses as the craze initiation and shear band initiation stresses, respectively.

As shown in Fig. 4, PS exhibits the essentially same temperature dependencies for both the craze initiation and fracture stress curves in the brittle fracture region. A similar correlation can be seen for the set of shear band initiation and yield stresses in the ductile fracture region. However, these two sets of curves show quite different temperature dependencies and, furthermore, they intersect in the temperature region where the brittle to ductile transition was observed. Another characteristic point in Fig. 4 is that the craze initiation stress shows a substantial lowering around 35°C and the temperature dependency becomes much higher above that temperature. Haward et al.[24] observed similarly the irregular temperature dependence of the craze initiation stress in PS at the same temperature range (see Fig. 3 in Ref. 24), although they did not notice this phenomenon. The possibility that this irregular behavior might relate to the [illegible]-relaxation in PS will be discussed later.

For PMMA the temperature dependencies of these various stresses are shown in Fig. 5. Similar to the case of PS, the curve of craze initiation stress intersects with that of shear band initiation stress at the brittle to ductile transition temperature. However, the temperature dependencies of these stresses above and below the transition do not show much difference and the shear band initiation stress in the brittle fracture region estimated by the extrapolation of the curve seems to be only 10 to 20% higher than the observed craze initiation stress. From the combination of this estimation and the reported fact[6,7] that the crazes produce highly stress-concentrated portions at the craze tips, it is reasonable to deduce that the shear band initiates just after the occurrence of craze formation in this temperature region of 40 to -10°C and thus supresses the further development of crazes. This phenomenon might be the reason why PMMA shows only a few crazes and does not exhibit the craze-yielding on the stress-strain curves typical of PS.

It is noticeable that the brittle to ductile transition temperatures observed in this study, which agree well with the reported transition temperatures of 90°C for PS[25] and 40-45°C for PMMA[3,26], are located very closely to the α-relaxation temperature of PS and β-one of PMMA, respectively. As a consequence, it has been suggested[9-11] that these two polymers are good examples of a clear correlation between the brittle to ductile transition and these mechanical relaxation phenomena. However, it will be proved in the next section that this good correlation does not exist for either polymer when they are tested under a hydrostatic pressure environment.

Pressure and Temperature Dependencies on the Brittle to Ductile Transition

As has been reported[17,18], the superposition of hydrostatic pressure on the tensile specimen can induce a brittle to ductile transition at room temperature. Figure 6 shows the pressure effects on the stress-strain curves of PS tested at constant temperature of 31°C[17]. The fracture mode of PS changes from brittle to ductile between 0.3 kb and 0.4 kb, while the Young's modulus increases almost continuously with pressure. The stress-strain curves were analyzed in the manner described in the preceding section and the obtained pressure dependencies of characteristic stresses are shown in Fig. 7. Although at atmospheric pressure the craze initiation stress is much lower than the shear band initiation stress, the superposition of hydrostatic pressure raises the stress necessary for the onset of crazing more rapidly than that for the onset of shear band formation and these two stresses become equal at the brittle to ductile transition pressure. Quite similarily, PMMA has been proved to exhibit its brittle to ductile transition between 0.2 kb and 0.3 kb at 23°C[18].

The above observations demonstrate that the brittle to ductile transition in amorphous polymers can be induced either by the raising of experimental temperature or by the superposition of hydrostatic pressure. However, a deeper knowledge of how these two individual phenomena are connected to each other is not immediately apparent. In this regard, to investigate how the experimental temperature affects the brittle to ductile transition pressure offers a possible approach to understand the fundamental mechanism controlling the brittle to ductile transition phenomenon in amorphous polymers. To study the temperature effects on the mechanical behaviors in PS and PMMA under pressure, the tensile experiments have been carried out under pressure and at various temperatures of 5, 20, 31, 40 and 50°C for PS and -10, 5, 23, 30, and 40°C for PMMA.

The resulting pressure effects on the stress-strain curves of PS at 5°C are shown and compared in Fig. 8 with those for specimens tested at the higher temperature of 40°C. It is obvious that the increase of the experimental temperature lowers the brittle to ductile transition pressure as well as the characteristic stresses, such as fracture stress and yield stress, and also the Young's modulus. At 5°C, PS fractures in a brittle manner up to 0.8 kb, but the fracture mode changes to ductile above 0.9 kb. As the temperature is raised, the brittle to ductile transition pressure becomes lower and lower, and the transition appears between 0.4 kb and 0.5 kb at 40°C. Similar temperature effects can be also observed in PMMA, as shown in Fig. 9. PMMA exhibits the brittle to ductile transition between 0.3 kb and 0.4 kb at -10°C, while the transition appears below 0.1 kb when the tensile expriments are performed at higher temperature of 40°C.

The stress-strain curves of the specimens tested under pressure and at different temperatures have been analyzed and the pressure dependencies of the craze initiation and shear band initiation stresses at various temperatures are shown in Fig. 10 for PS and in Fig. 11 for PMMA, respectively. It is again noticeable that the two curves for the craze initiation and shear band initiation stresses intersect at the brittle to ductile transition pressure irrespective of the test temperature for the both cases of PS and PMMA.

Based on the data given in Figs. 10 and 11, the pressure and temperature dependencies of craze initiation stress ($d\sigma_{ci}/dP$ and $d\sigma_{ci}/dT$) and those of shear band initiation stress ($d\sigma_{sb}/dP$ and $d\sigma_{sb}/dT$) are calculated and the values are listed in Table I. Since these values vary with the temperature and/or pressure, the table lists the values averaged over the examined temperature and/or pressure regions. From the comparisons of the data on the pressure and temperature dependencies, it is apparent that craze formation is much more suppressed by the increase of the superposed pressure than is shear band formation (i.e. $(d\sigma_{ci}/dP)/(d\sigma_{sb}/dP) > 1$). In contrast, increased temperature affects shear band initiation process more strongly than crazing (i.e. $(d\sigma_{ci}/dT)/(d\sigma_{sb}/dT) < 1$). These results demonstrate that the crazing and shear banding phenomena have different sensitivities to the changes in environmental pressure and temperature, which is in keeping with the view that very different rather than similar super molecular processes are involved in these two phenomena. This point is examined further in the next section.

Figure 12 shows the temperature dependencies of the brittle to ductile transition pressure obtained from the stress-strain measurements.

Both polymers -- PS and PMMA -- show a similar general trend in that the brittle to ductile transition pressure becomes higher with decreasing temperature. This temperature dependency of the transition pressure, however, is the inverse of that expected from the concept that the brittle to ductile transition relates to mechanical relaxation phenomena, because the temperatures of both the mechanical α- and β-relaxations are known to become higher with increasing pressure. The reasons for this discrepancy and for the irregular temperature dependency of the transition pressure observed in PS around 40°C, will be discussed in detail in the next section.

DISCUSSION

From the tensile experiments of PS and PMMA under the wide range of pressure and temperature performed in this study, the following general features may be attributed to the brittle to ductile transition phenomenon in amorphous polymers: (1) The pressure dependence of the craze initiation stress is considerably higher than that of the shear band initiation stress. (2) The temperature dependence of the craze initiation stress is considerably lower than that of the shear band initiation stress. (3) The two curves of the craze initiation stress and the shear band initiation stress intersect at the point where the brittle to ductile transition (whether pressure or temperature) is observed and the craze initiation stress always becomes higher than the shear band initiation stress above this transition point. (4) The brittle to ductile transition pressure becomes higher with decreasing temperature, and conversely the transition temperature becomes lower with increasing pressure.

While the items (1) and (2) suggest that the crazing and shear banding phenomena have quite different formation mechanisms, Brady and Yeh[27] have reported that there exist several similarities between the craze morphology and shear band morphology in PS. However, the fact that the superposition of hydrostatic pressure affects the crazing more than the shear banding is in accord with the well-established difference in their formation mechanisms whereby the crazing involves void formation but shear banding essentially does not. Moreover the larger temperature dependency of the shear banding over the crazing implies that the molecular motions associated with the banding, such as molecular sliding[23], can be enhanced by the increase in temperature much more than the molecular motions for craze formation.

From the item (3), a satisfactory explanation can be deduced for the general mechanism of the brittle to ductile transition phenomenon, whether the transition is induced either by the increase of temperature or by the superposition of pressure. The explanation is simply that the material fractures in a brittle manner if the crazes can initiate at lower stress level than the shear bands at the test conditions of temperature and pressure. If they cannot, the fracture mode will be ductile because the shear bands that form before the initiation of the craze function so as to suppress the initiation of new crazes or propagation of existing crazes[28-30] which normally lead the specimen to the brittle fracture. Thus, the competition of and interaction between the crazing and shear banding play a particularly important part in the brittle to ductile transition phenomenon in amorphous polymers.

Further, this concept of the transition mechanism provides the answer as to why the temperature dependencies of the brittle to ductile pressure in PS and PMMA differ from that expected from the idea that the transition relates to the mechanical relaxation phenomena. As described above, the brittle to ductile transition phenomenon is caused by the interaction between two independent <u>plastic deformations</u> of crazing and shear banding, and is not due to a direct effect of the mechanical relaxation motions. Therefore, the brittle to ductile transition point depends upon how the changes of pressure and/or temperature affect the craze initiation and shear band initiation processes and hence shift the intersection point of the initiation stresses for these two processes.

In this regard, there exists no reason to expect the brittle to ductile transition to shift with the changes in pressure and/or temperature so as in the same manner as do the mechanical relaxation processes.

Despite this absence of a direct effect of relaxations on the brittle to ductile transition, there are some secondary or indirect effects in the case of the β-relaxation in PS. As shown in Fig. 12 and more clearly in Fig. 13, the brittle to ductile transition pressures in PS change irregularly with decreasing temperature around 40°C. At atmospheric pressure, the craze initiation stress curve of PS showed the irregular lowering around 35°C (Fig. 4), which is very close to the reported β-relaxation temperature range of 25-60°C[31]. Further, Boyer[32] found from the analysis of Maxwell and Rahm's data[33] on the crazing that the apparent activation energy of the β-relaxation in PS agrees with the activation energy for the crazing. Therefore, above the β-relaxation temperature, if this β-relaxation really enhances the formation of crazes in PS, it could be expected that the stress necessary to initiate crazes will become substantially lower and hence brittle fracture will be more favored. Naturally, the brittle to ductile transition phenomenon under pressure will be also influenced indirectly by the existence of such β-relaxation and the pressure necessary to induce the transition will become discontinuously higher in order to compensate for the substantial lowering in the craze initiation stress. As demonstrated in Fig. 13, where the pressure dependency of the β-relaxation temperature is assumed to be about 4°C/kb, (by analogy with PMMA[34]) the discontinuous increase in the brittle to ductile transition pressure is actually observed at the region where the transition curve meets with the β-relaxation curve. Thus, the hypothesis that the β-relaxation in PS lowers the craze initiation stress and indirectly affects the brittle to ductile transition process can explain simultaneously the both experimental facts of the irregular lowering of craze initiation stress observed at atmospheric pressure and the irregular region of the temperature dependency of the transition pressure.

In contrast to PS, the pressure-temperature characteristic for PMMA do not show irregularities, despite Boyer[32] interpreted that the β-relaxation in PMMA is also associated with the crazing phenomenon. The experimental results, however, do not give any distinct evidence for a relationship between the β-relaxation and the craze initiation stress curve and/or the brittle to ductile transition curve in this polymer. Rather, PMMA exhibits at atmospheric pressure its brittle to ductile transition at about 45°C near to the reported β-relaxation temperatures[35,36]. It is possible that this near coincidence of the latter with the transition temperature at atmospheric pressure, is preventing experimental observation of its effect.

CONCLUSIONS

Tensile experiments on PS and PMMA conducted over a wide range of pressure and temperature have shown that the brittle to ductile transition in these amorphous polymers is strongly affected by both the pressure and by the temperature. By using detailed stress-strain analyses, the pressure and temperature dependencies of the craze initiation and the shear band initiation processes were elucidated as the fundamental processes controlling the mechanism of the brittle to ductile transition. The major conclusions of this study may be summarized as follows:

(1) Pressure affects the craze initiation stress considerably more than the shear band initiation stress. However, temperature acts in exactly the opposite manner.

(2) These two initiation stresses become equal at the brittle to ductile transition pressure and/or temperature, suggesting that the transition is induced by the interaction between competing micro-plastic deformation processes -- crazing and shear banding.

(3) The brittle to ductile transition pressure decreases with increasing temperature due to the quite different pressure and temperature dependencies of the craze initiation and the shear band initiation stresses.

(4) This transition is not dependent on mechanical relaxation phenomena.

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FIGURE CAPTIONS

Fig. 1. Effect of temperature on the stress-strain behavior of PS at atmospheric pressure.

Fig. 2. Effect of temperature on the stress-strain behavior of PMMA at atmospheric pressure.

Fig. 3. Typical stress-strain curves for the brittle fracture without (PMMA) and with craze-yielding (PS) and the ductile fracture. An inflection point on the stress-strain curve for the brittle fracture corresponds to the craze initiation point. That for the ductile fracture corresponds to the shear band initiation point.

Fig. 4. Temperature dependencies of the craze initiation, shear band initiation, fracture, and yield stresses in PS. Arrow BD indicates the brittle to ductile transition point.

Fig. 5. Temperature dependencies of the craze initiation, shear band initiation, fracture, and yield stresses in PMMA. Arrow BD indicates the brittle to ductile transition point.

Fig. 6. Effect of pressure on the stress-strain behavior of PS at 31°C.

Fig. 7. Pressure dependencies of the craze initiation, shear band initiation, fracture, and yield stresses in PS at 31°C. Arrow BD indicates the brittle to ductile transition point.

Fig. 8. Effect of pressure on the stress-strain behavior of PS at different temperatures of 5°C and 40°C.

Fig. 9. Effect of pressure on the stress-strain behavior of PMMA at different temperatures of -10°C and 40°C.

Fig. 10. Pressure dependencies of the craze initiation stress and the shear band initiation stress in PS at different temperatures of 5, 20, 31, 40, and 50°C.

Fig. 11. Pressure dependencies of the craze initiation stress and the shear band initiation stress in PMMA at different temperatures of -10, 5, 23, and 40°C.

Fig. 12. Temperature dependencies of the brittle to ductile transition pressure in PS and PMMA.

Fig. 13. Influence of the β-relaxation on the temperature dependency of the brittle to ductile transition pressure in PS.

Table I. Comparison of the pressure and temperature dependencies of the craze initiation stress (σ_{ci}) and the shear band initiation stress (σ_{sb}) in PS and PMMA.

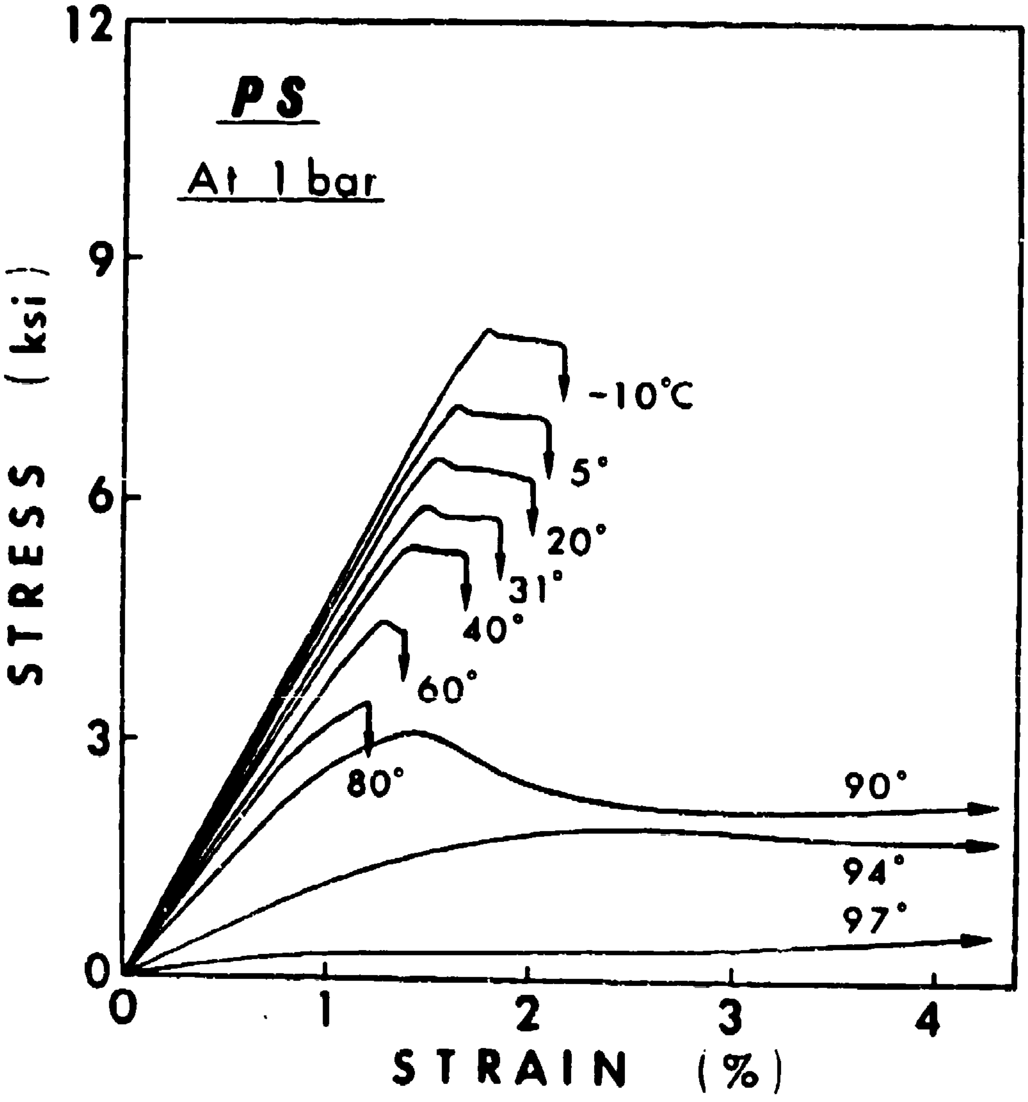

Figure 1. Effect of temperature on the stress-strain behavior of PS at atmospheric pressure.

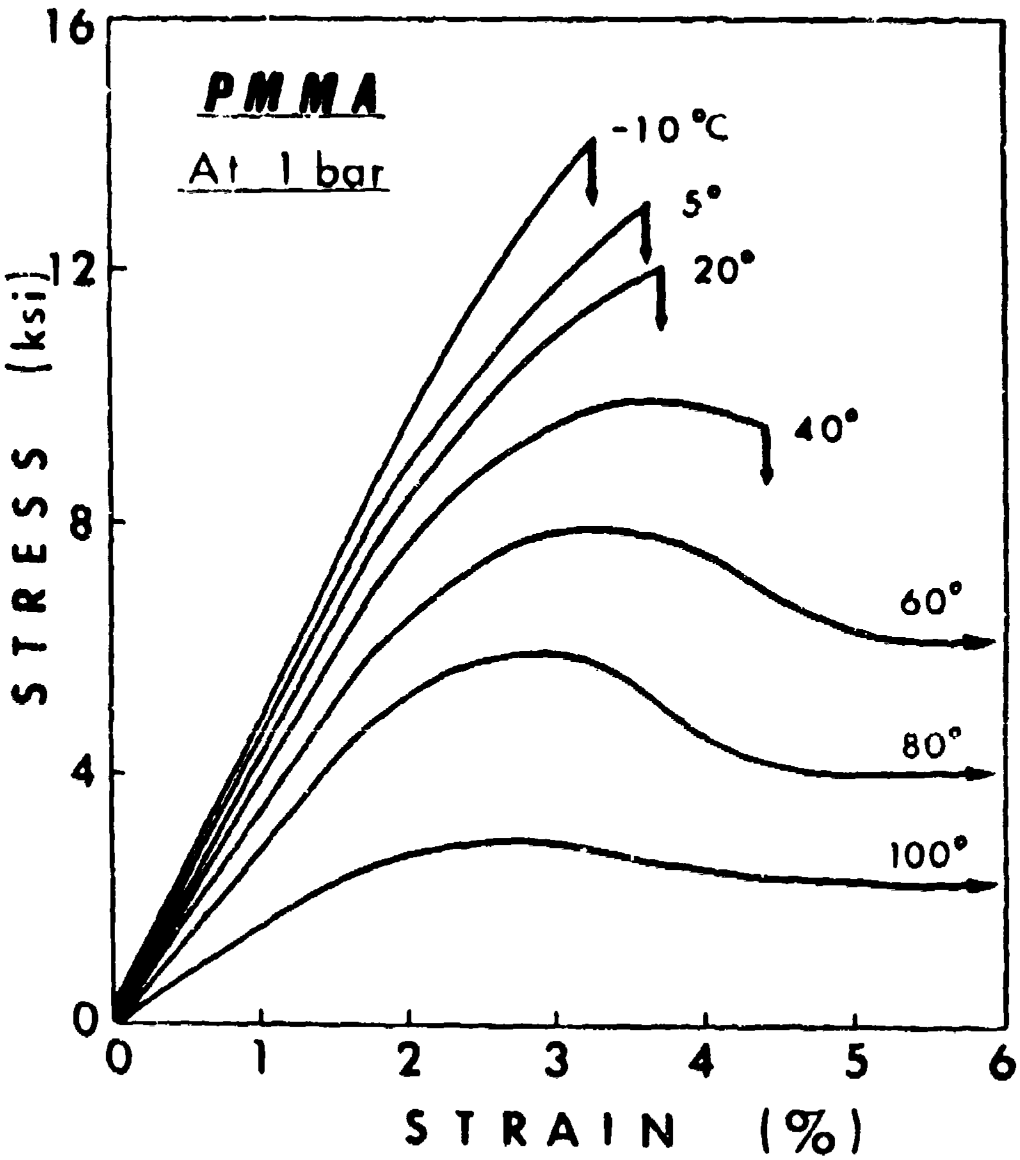

Figure 2. Effect of temperature on the stress-strain behavior of PMMA at atmospheric pressure.

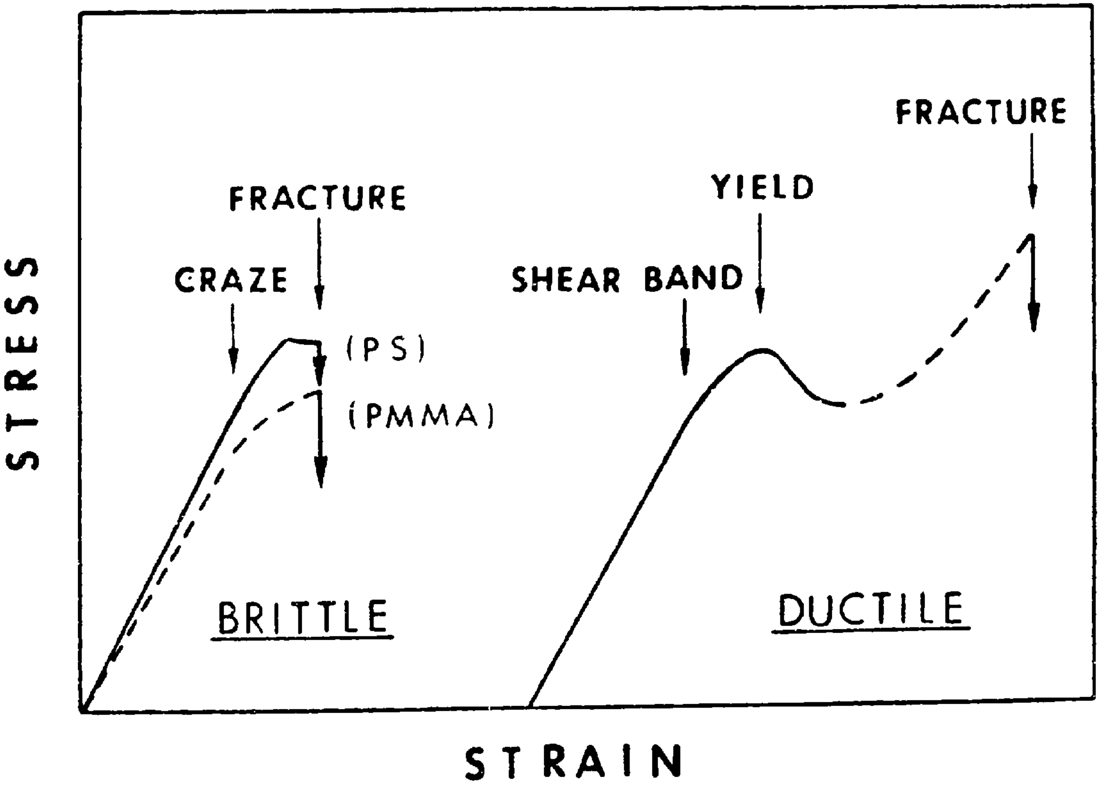

Figure 3. Typical stress-strain curves for the brittle fracture without (PMMA) and with craze-yielding (PS) and the ductile fracture. An inflection point on the stress-strain curve for the brittle fracture corresponds to the craze initiation point. That for the ductile fracture corresponds to the shear band initiation point.

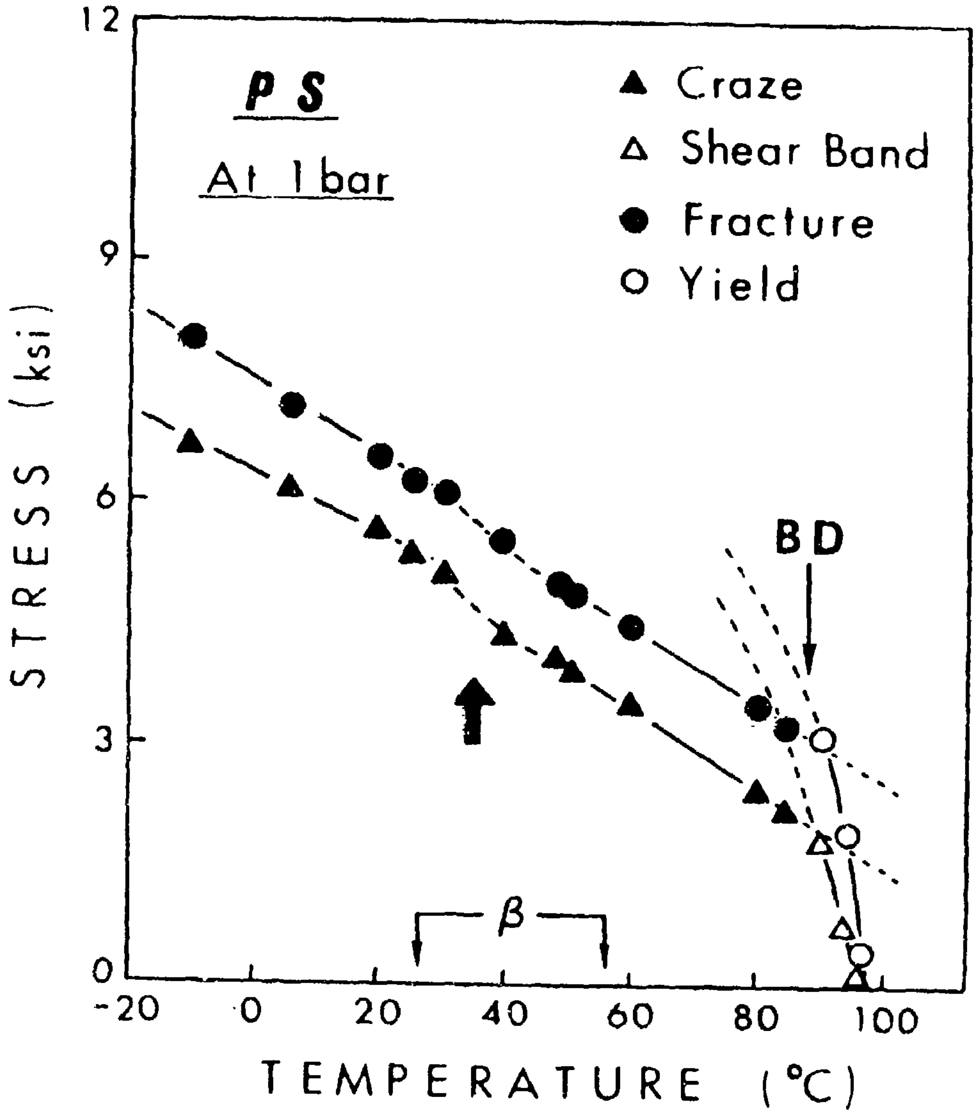

Figure 4. Temperature dependencies of the craze initiation, shear band initiation, fracture, and yield stresses in PS. Arrow BD indicates the brittle to ductile transition point.

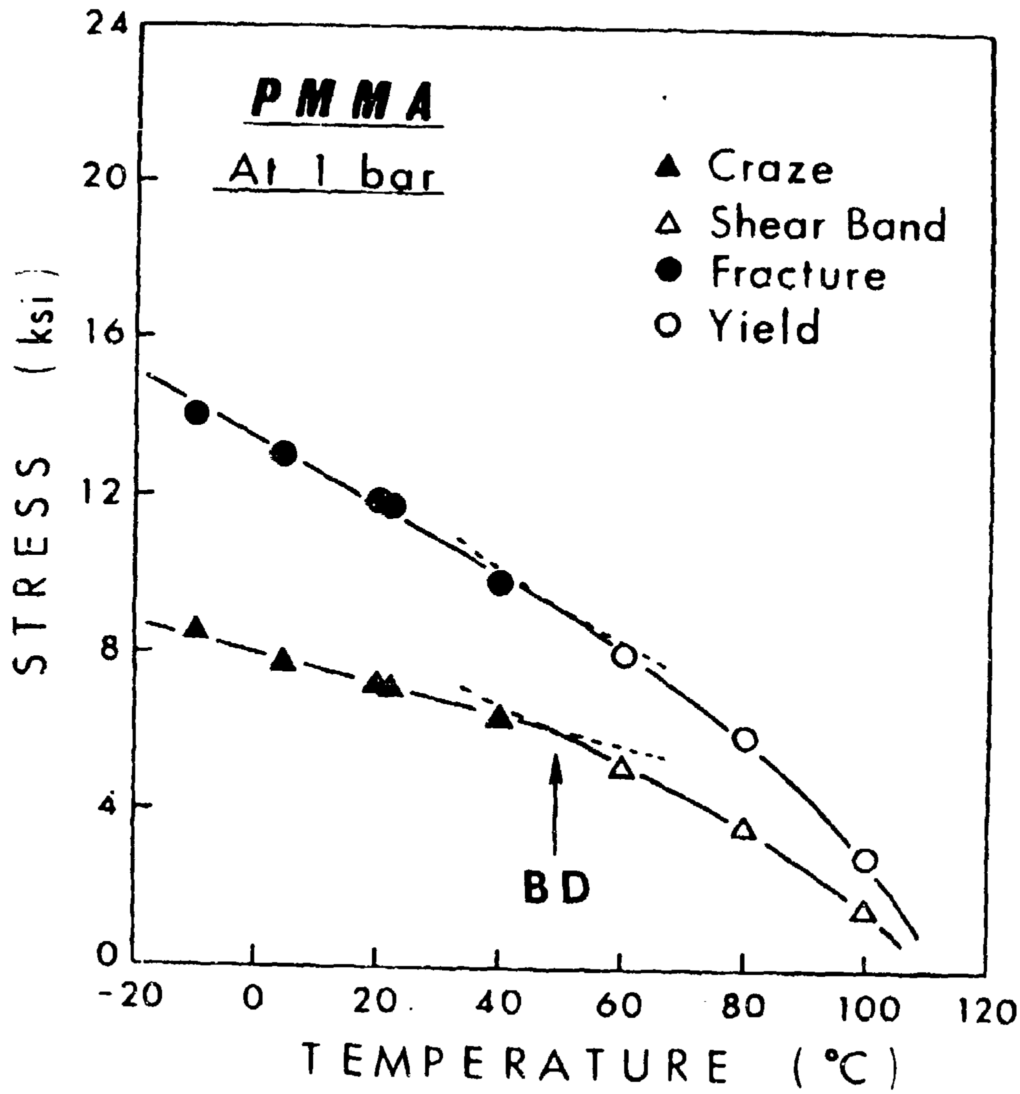

Figure 5. Temperature dependencies of the craze initiation, shear band initiation, fracture, and yield stresses in PMMA. Arrow BD indicates the brittle to ductile transition point.

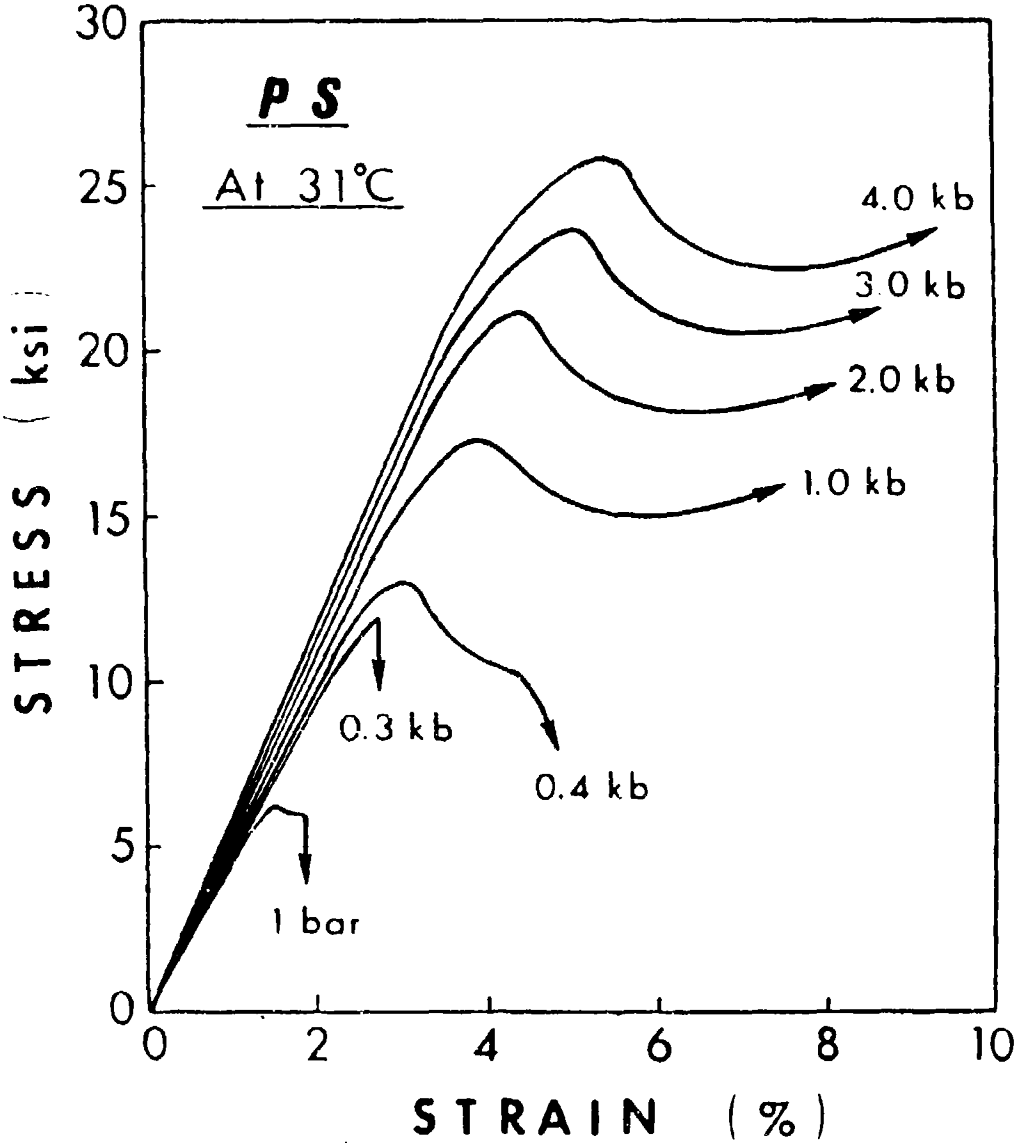

Figure 6. Effect of pressure on the stress-strain behavior of PS at 31°C.

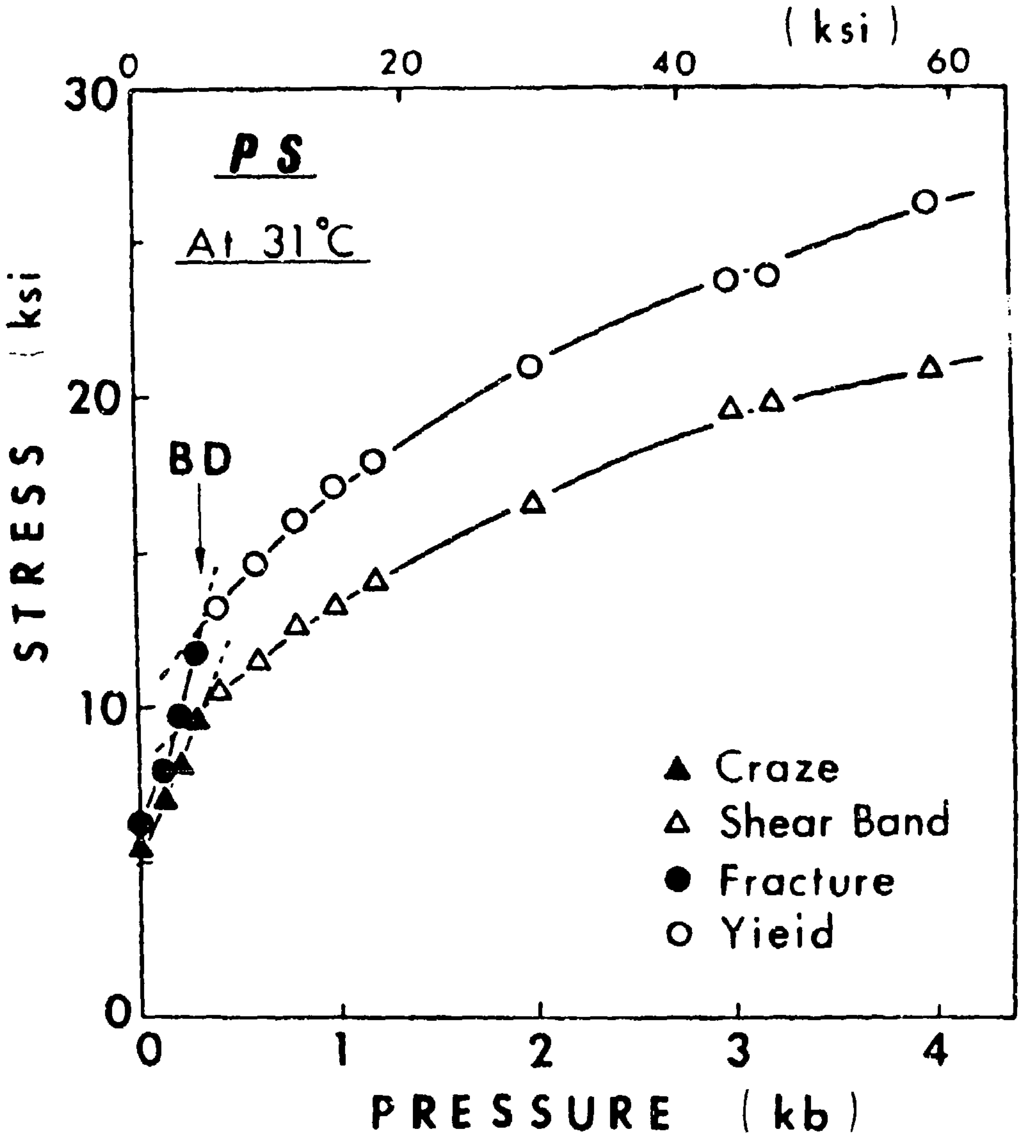

Figure 7. Pressure dependencies of the craze initiation, shear band initiation, fracture, and yield stresses in PS at 31°C. Arrow BD indicates the brittle to ductile transition point.

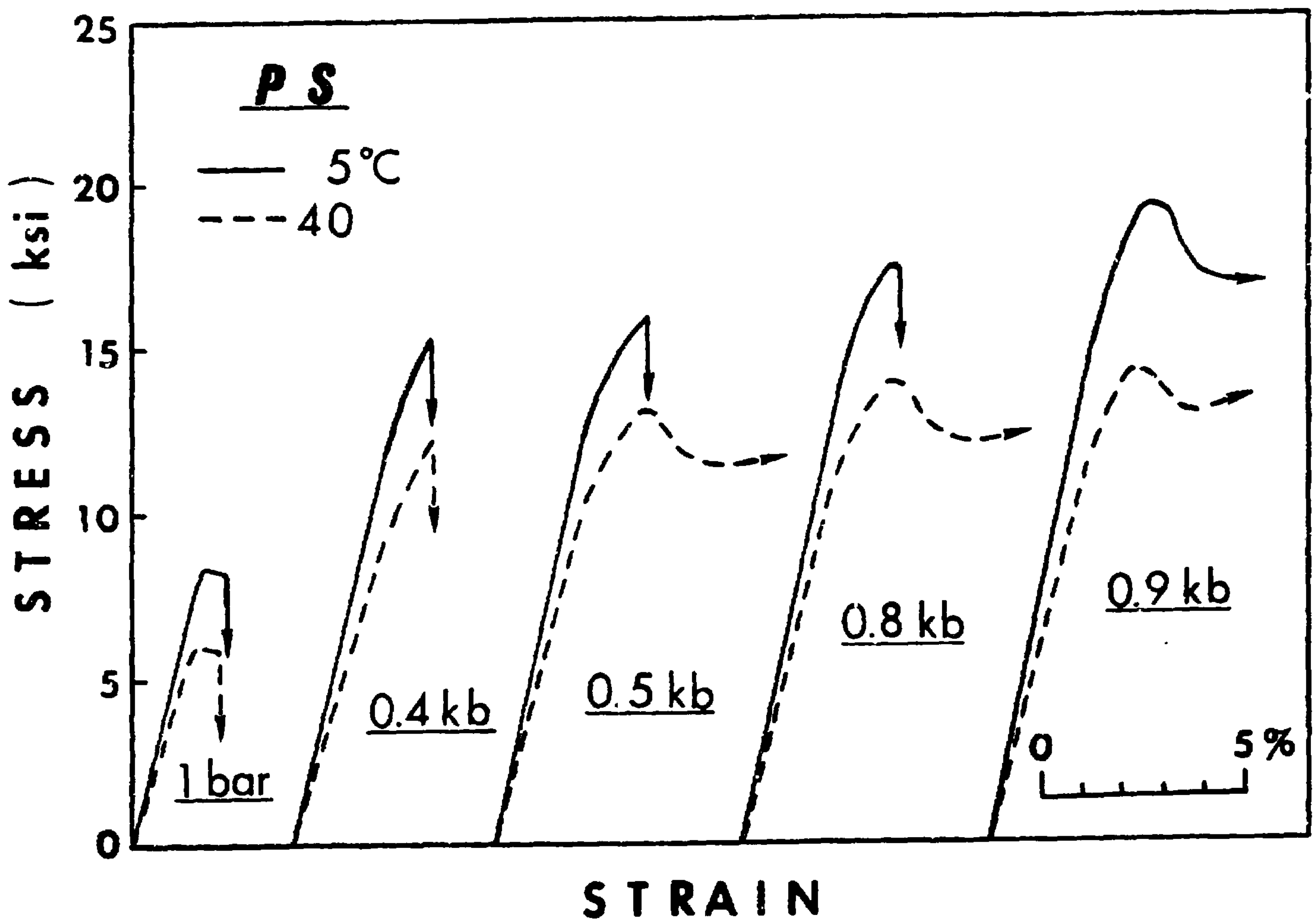

Figure 8. Effect of pressure on the stress-strain behavior of PS at different temperatures of 5°C and 40°C.

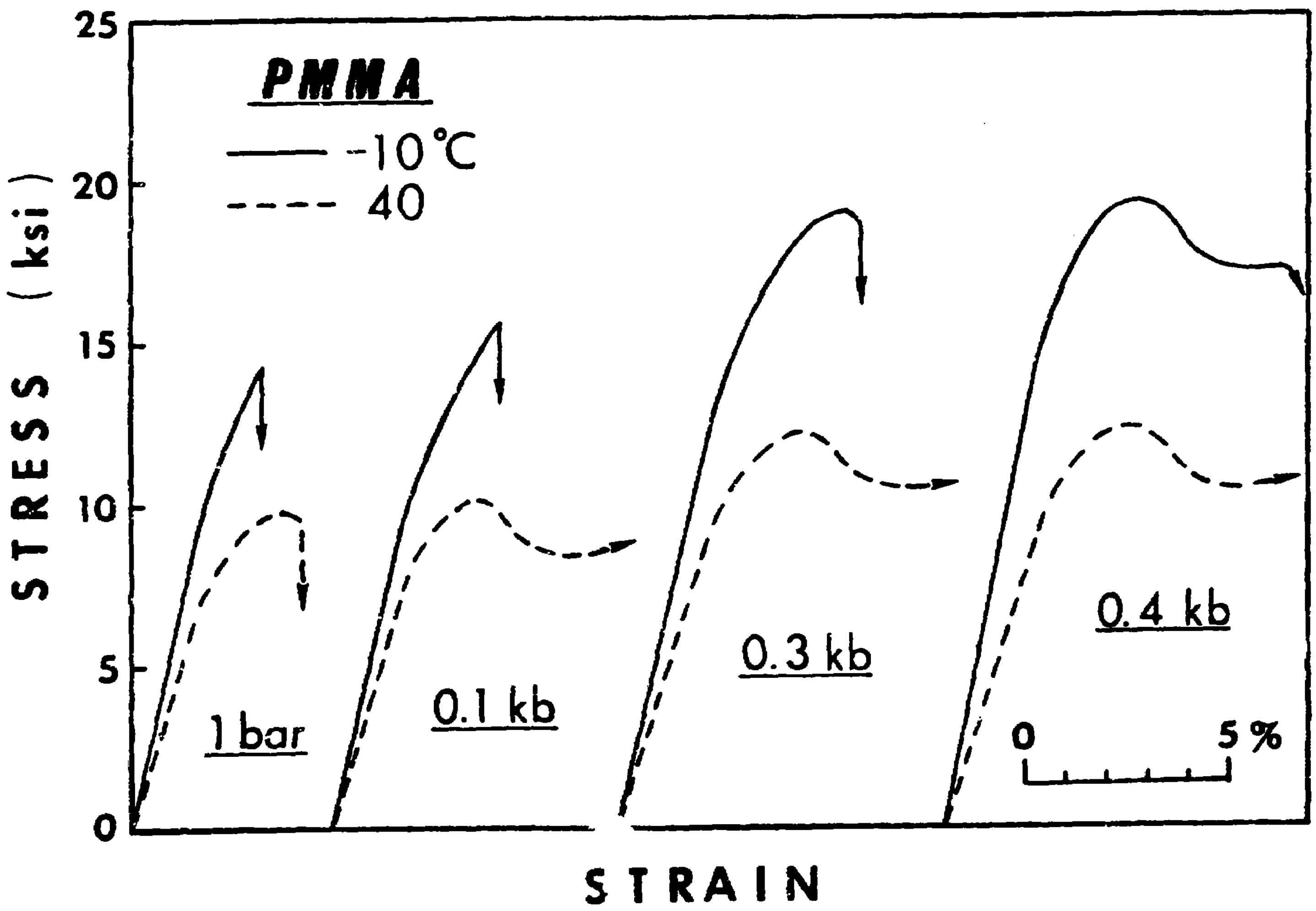

Figure 9. Effect of pressure on the stress-strain behavior of PMMA at different temperatures of -10°C and 40°C.

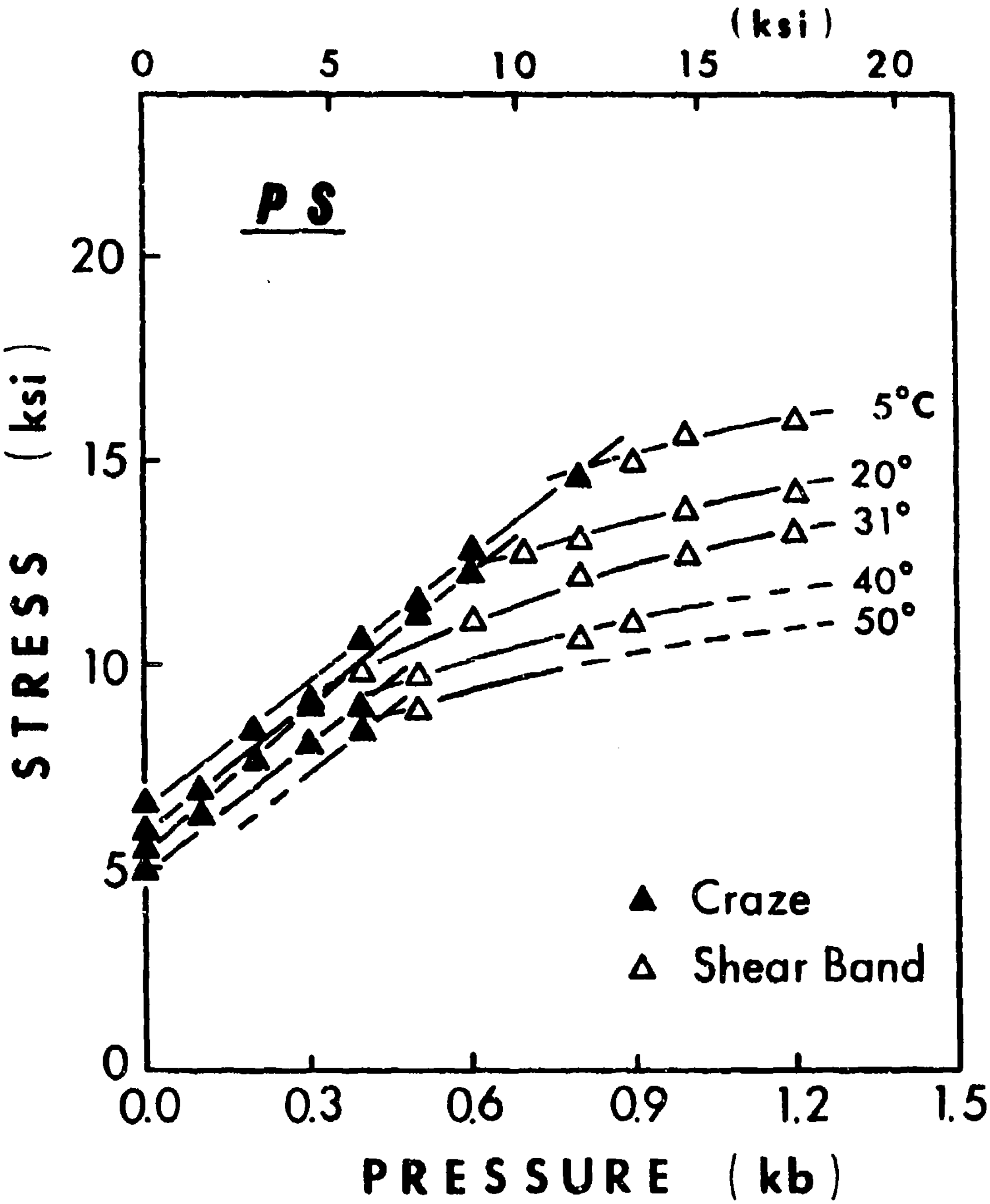

Figure 10. Pressure dependencies of the craze initiation stress and the shear band initiation stress in PS at different temperatures of 5, 20, 31, 40, and 50°C.

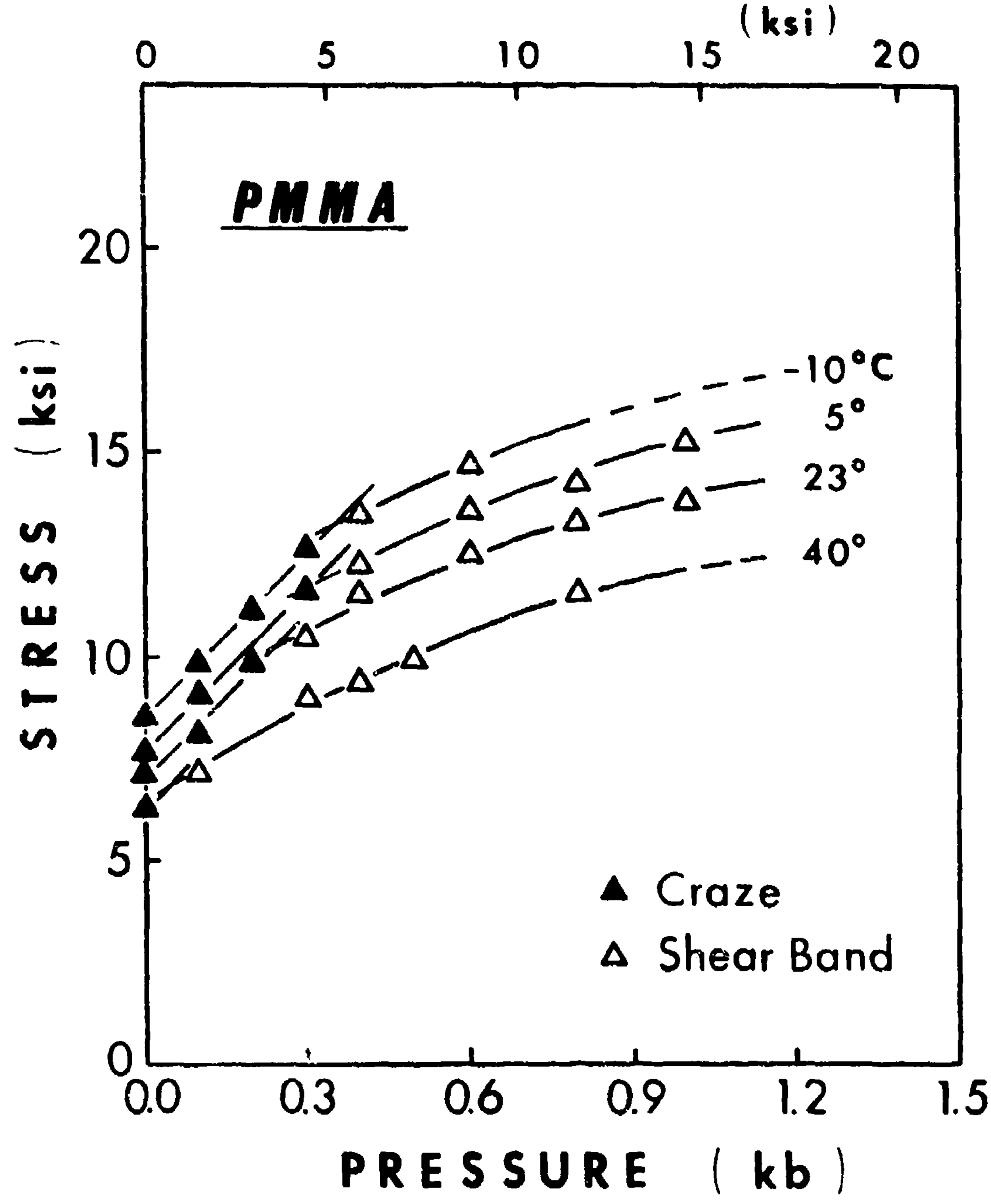

Figure 11. Pressure dependencies of the craze initiation stress and the shear band initiation stress in PMMA at different temperatures of -10, 5, 23, and 40°C.

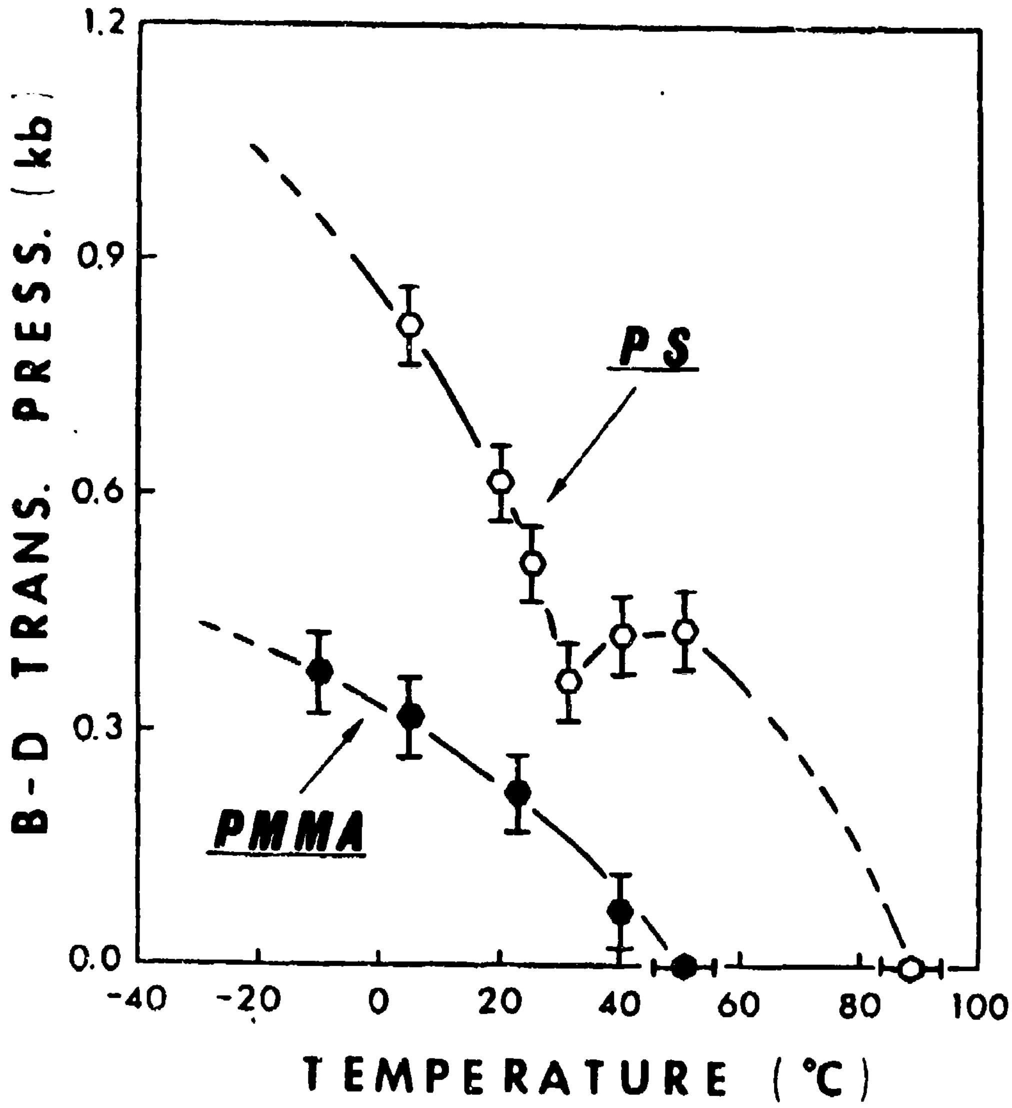

Figure 12. Temperature dependencies of the brittle to ductile transition pressure in PS and PMMA.

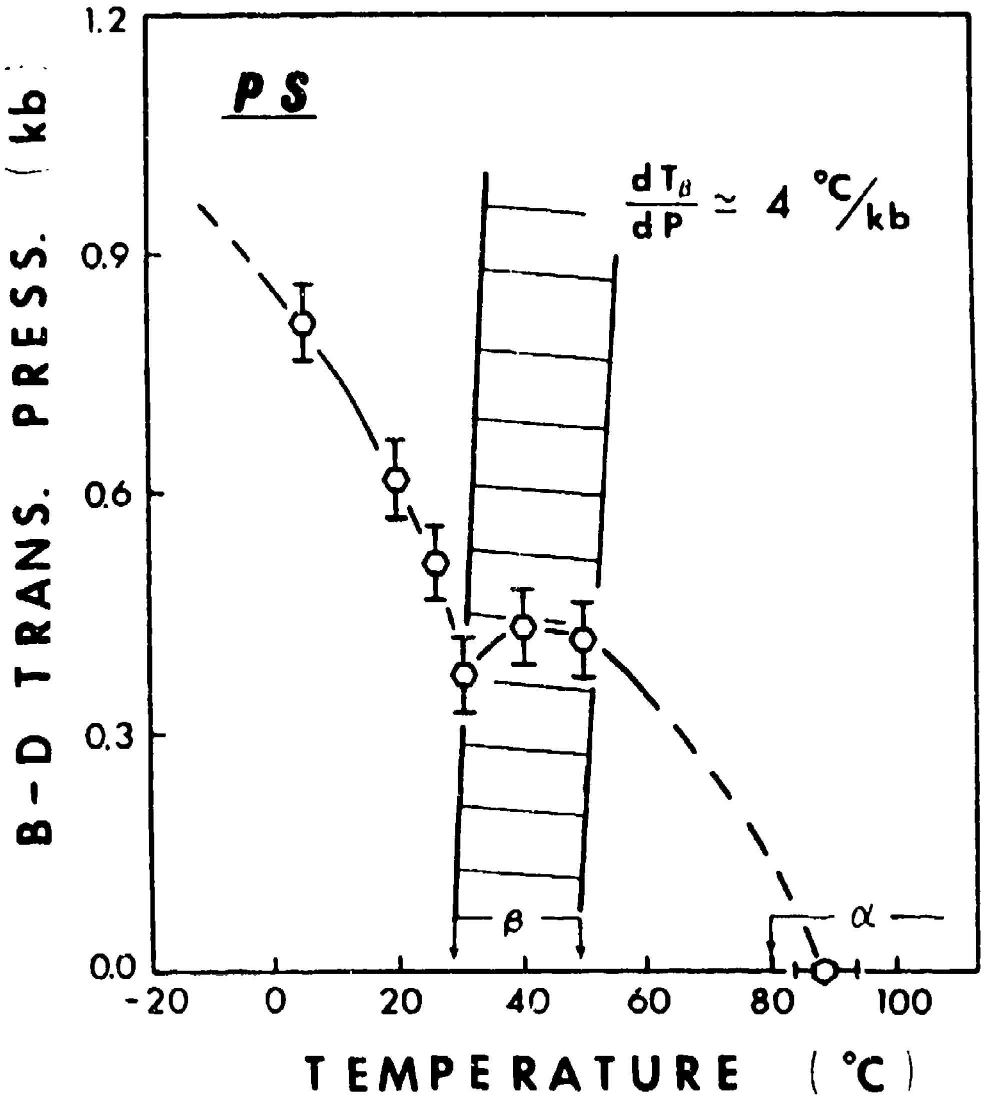

Figure 13. Influence of the β-relaxation on the temperature dependency of the brittle to ductile transition pressure in PS.

	$\frac{d\sigma_{ci}}{dP}$	$\frac{d\sigma_{sb}}{dP}$	$(\frac{d\sigma_{ci}}{dP})/(\frac{d\sigma_{sb}}{dP})$	$\frac{d\sigma_{ci}}{dT}$	$\frac{d\sigma_{sb}}{dT}$	$(\frac{d\sigma_{ci}}{dT})/(\frac{d\sigma_{sb}}{dT})$
PS	11	4	2.7	-0.2	-1.1	0.18
PMMA	13	6	2.2	-0.5	-0.8	0.63
	(ksi/kb)			(ksi/°C)		

Table I. Comparison of the pressure and temperature dependencies of the craze initiation stress (σ_{ci}) and the shear band initiation stress (σ_{sb}) in PS and PMMA.